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# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: A01N 37/50 // (A01N 37/50, 57:20, 55:00, 47:38, 47:34, 47:24, 47:18, 47:04, 43:88, 43:84, 43:82, 43:78, 43:76, 43:653, 43:56, 43:54, 43:50, 43:42, 43:40, 43:36, 43:30, 43:08, 37:52, 37:50, 37:46, 37:38, 37:34, 37:24, 37:20)

WO 99/11125 (11) International Publication Number:

11 March 1999 (11.03.99) (43) International Publication Date:

(21) International Application Number:

PCT/EP98/05453

A1

(22) International Filing Date:

27 August 1998 (27.08.98)

(30) Priority Data:

9718366.9

29 August 1997 (29.08.97)

GB

(71) Applicant (for all designated States except AT US): NOVAR-TIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(71) Applicant (for AT only): NOVARTIS-ERFINDUNGEN VER-WALTUNGSGESELLSCHAFT M.B.H. [AT/AT]; Brunner Strasse 59, A-1235 Vienna (AT).

(72) Inventors; and

KNAUF-BEITER, (75) Inventors/Applicants (for US only): Gertrude [DE/DE]; Fritz-Fischerstrasse 12, D-79379 Müllheim (DE). ZURFLÜH, René [CH/CH]; Waldenburgerstrasse 1, CH-4052 Basel (CH). GSELL, Bettina [CH/CH]; Schachenweg 6, CH-8610 Uster (CH).

(74) Agent: BECKER, Konrad; Novartis AG, Patent- und Markenabteilung, Lichtstrasse 35, CH-4002 Basel (CH).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: FUNGICIDAL COMBINATIONS COMPRISING PHENYLACRYLIC ACID DERIVATIVES

$$C = N - O - CH_3$$

$$C = N - O - CH_3$$

$$CH_2 - O - N = C$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$C = N - O - CH_3$$

(57) Abstract

A method of combatting phytopathogenic diseases on crop plants which comprises applying to the crop plants or the locus thereof being infested with said phytopathogenic disease an effective amount of a combination of: a) a 2-(5-phenyl-3,6-diaza-2,7-dioxa-octa-3,5-dienyl)-phenylacrylamide of formula (I) wherein R<sub>1</sub> is hydrogen, fluoro or chloro, R<sub>2</sub> is methyl, ethyl, trifluoromethyl, trifluoromethoxy, cyano, fluoro, chloro or bromo, with the proviso that R<sub>2</sub> cannot be fluoro, chloro or bromo, when R<sub>1</sub> is hydrogen; in association with b) a broad variety of other plant fungicides is particularly effective in combatting or preventing fungal diseases of crop plants. These combinations exhibit synergistic fungicidal activity.

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# FUNGICIDAL COMBINATIONS COMPRISING PHENYLACRYLIC ACID DERIVATIVES

The present invention relates to novel fungicidal compositions for the treatment of phytopathogenic diseases of crop plants, especially phytopathogenic fungi, and to a method of combating phytopathogenic diseases on crop plants.

It is known that certain 2-(5-phenyl-3,6-diaza-2,7-dioxa-octa-3,5-dienyl)-phenylacrylic acid derivatives have biological activity against phytopathogenic fungi, e.g. known from WO 95/18789, WO 95/21154 and WO 97/20809 where their properties and methods of preparation are described. On the other hand azole derivatives, phthalimides, phenylamides, morpholines and aminopyrimidines and numerous further compounds of different chemical classes are widely known as plant fungicides for application in various crops of cultivated plants. However, crop tolerance and activity against phytopathogenic plant fungi do not always satisfy the needs of agricultural practice in many incidents and aspects.

It has now been found that the use of

a) a 2-(5-phenyl-3,6-diaza-2,7-dioxa-octa-3,5-dienyl)-phenylacrylamide of formula I

$$CO-NH\cdot CH_3$$

$$C=N-O-CH_3$$

$$CH_2-O-N$$

$$CH_3$$

wherein

R<sub>1</sub> is hydrogen, fluoro or chloro,

 $R_2$  is methyl, ethyl, trifluoromethyl, trifluoromethoxy, cyano, fluoro, chloro or bromo, with the proviso that  $R_2$  cannot be fluoro, chloro or bromo, when  $R_1$  is hydrogen; in association with

b) either an anilinopyrimidine of formula II

wherein

R<sub>3</sub> is methyl, 1-propynyl or cyclopropyl; or an azole of formula III

$$R_4$$
 $A$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 
 $N$ 

wherein

A is selected from

(ii) 
$$\frac{1}{\beta} = \frac{1}{C - CH_2}$$
, (iii)  $\frac{1}{\beta} = \frac{C - CH_2}{CR_6R_7R_8}$  (iv)  $\frac{C}{\beta} = \frac{C}{CH_2}$  (iv)  $\frac{C}{C} = \frac{C}{C}$  (iv

$$(v) \quad \frac{\bigcap\limits_{\beta}^{OH} C - CH_{2}}{\bigcap\limits_{R_{9}}^{C} CH_{2}} \quad , \quad (vi) \quad \frac{\bigcap\limits_{\beta}^{O} CH - CH_{2}}{\bigcap\limits_{R_{9}}^{C} CH_{2}} \quad ,$$

(vii) 
$$CH_2 - CH_2 - C$$

$$(ix) \qquad \frac{CH - CH_{2}}{\beta} \qquad (x) \qquad \frac{R_{8}}{\beta} \qquad CH_{2}$$

$$(xi) \qquad \frac{CH}{\beta} \qquad CH_{2} \qquad (xii) \qquad \frac{CH}{\beta} \qquad CH = C - CH_{2}$$

$$(xiii) \qquad \frac{CH}{\beta} \qquad (xiii) \qquad \frac{CH}{\beta} \qquad CH_{2} \qquad CH_{2} \qquad and$$

$$(xiiii) \qquad \frac{G}{\beta} \qquad (xiv) \qquad \frac{C}{\beta} \qquad CH_{2} \qquad and$$

$$(xiv) \qquad \frac{C}{\beta} \qquad CH_{2} \qquad and$$

$$(xiv) \qquad \frac{CH}{\beta} \qquad CH_{2} \qquad and$$

$$(xiv) \qquad \frac{CH}{\beta} \qquad CH_{2} \qquad and$$

whereby the  $\beta$ -carbon attaches to benzene ring of formula III, and wherein

R<sub>4</sub> is H, F, Cl, 4-fluorophenoxy or 4-chlorophenoxy;

R<sub>5</sub> is H, Cl or F;

 $R_6$  and  $R_7$  are independently H or  $CH_3$ ;

R<sub>8</sub> is C<sub>1-4</sub>alkyl or cyclopropyl;

 $R_9$  is 4-chlorophenyl or 4-fluorophenyl;

R<sub>10</sub> is phenyl, and

 $R_{11}$  is allyloxy,  $C_{1-4}$ alkyl, or 1,1,2,2-tetrafluoroethoxy-methyl, and the salts of such azole fungicide;

or a morpholine fungicide of formula IV

$$H_3C$$

$$O$$

$$N-R_{12}$$

$$H_3C$$
(IV)

wherein

 $R_{12}$  is  $C_{8-15}$ cycloalkyl,  $C_{8-15}$ alkyl, or  $C_{1-4}$ alkylphenyl- $C_{1-4}$ alkyl, and the salts of such morpholine fungicide;

or a strobilurin compound of formula V

wherein

X is NH or O.

Y is CH or N, and

R<sub>13</sub> is 2-methylphenoxy-methyl, 2,5-dimethylphenoxy-methyl, 4-(2-cyanophenoxy)-pyrimidin-6-yloxy, or 4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl;

or a pyrrole compound of the formula VI

wherein

 $R_{14}$  and  $R_{15}$  are indendently halo, or together from a perhalomethylendioxo bridge; or a phenylamide of the formula VII

$$\begin{array}{c} CH_{3} \\ CO - R_{16} \\ \hline \\ CH_{3} \end{array}$$

wherein

R<sub>16</sub> is benzyl, methoxymethyl, 2-furanyl or chloromethyl,

 $R_{17}$  is 1-methoxycarbonyl-ethyl, or

Z is CH or N;

or a dithiocarbamate fungicide selected from mancozeb, maneb, metiram and zineb; or a copper compound selected from copper hydroxide, copper oxychloride, copper sulfate and oxine-copper;

or sulfur;

or a phthalimide compound of the formula VIII

$$\begin{array}{c|c} R_{18} & O \\ \hline N-S-CCI_3 \\ \hline R_{19} & O \end{array}$$

wherein

 $R_{18}$  and  $R_{19}$  together form a 4-membered bridge -CH2-CH=CH-CH2- or =CH-CH=CH-CH= ;

or with the compound of formula IX

$$CI \longrightarrow C_3H_7-n$$

$$CI \longrightarrow C_2CH_2-N-CO-N \longrightarrow N$$

$$CI \longrightarrow CI$$

$$CI \longrightarrow C_3H_7-n$$

$$CI \longrightarrow CI$$

or with the compound of formula X

$$CI \xrightarrow{CF_3} CH_2^-O - C_3H_7 - n$$

$$CI \xrightarrow{N} C$$

$$N = C$$

or with the compound of formula XI

or with the compound of formula XII

or with the compound of formula XIII

or with the compound of formula XIV

or with the compound of formula XV

$$C = CH - CO - NO$$
 (XV);

or with the compound of formula XVI

or with the compound of formula XVII

or with the compound of formula XVIII

or with the compound of formula XIX

$$F_3C$$
 $N$ 
 $N$ 
 $CI$ 
 $NO_2$ 
 $N$ 
 $CI$ 
 $NO_2$ 
 $CI$ 

or with the compound of formula XX

$$\begin{bmatrix} O \\ H_3C - CH_2 - P - OH \\ H \end{bmatrix}_3 AI$$
 (XX)

or with the compound of formula XXI

or with the compound of formula XXII

$$H_3C$$
 $CH_3$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_3$ 
 $CH_3$ 

or with the compound of formula XXIII

$$H_3C$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

or with the compound of formula XXIV

or with 2-chloro- N-(4'-fluoro-1,1'-biphenyl-2-yl)nicotinamide (compound XXV), or with 2-chloro- N-(4'-chloro-1,1'-biphenyl-2-yl)nicotinamide (compound XXVI), or with methyl N-(2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]phenyl)-N- methoxycarbamate (compound XXVII),

or with methyl N-(2-[1-(4-tolyl)pyrazol-3-yloxymethyl]phenyl)-N- methoxycarbamate (compound XXVIII),

or with 2-[4-methoxy-3-(1-methylethoxy)-1,4-diazabuta-1,3-dienyloxymethyl]phenyl-2-methoximino-N-methylacetamide (compound XXIX),

or with 2-[4-methoxy-3-(1-methylpropoxy)-1,4-diazabuta-1,3-dienyloxymethyl]phenyl-2-methoximino-N-methylacetamide (compound XXX),

or with N-(cyclopropylmethoxy)-N'-(2-phenylacetyl)-2,3-difluoro-6-trifluoromethylbenzamidine (compound XXXI),

or with N-[3'-(1'-chloro-3-methyl 2'-oxopentan)]-3,5-dichloro-4-methylbenzamide (compound XXXII),

or with methyl(2)-2-{6-[6-(trifluoromethyl)pyrid-2-yloxymethyl]-phenyl}-3-methoxyacrylate (compound XXXIII),

or with 2-chloro-4-(2-fluoro-2-methylpropionylamino)-N,N-dimethylbenzamide (compound XXXIV),

or with (S)-1-anilino-4-methyl-2-methylthio-4-phenylimidazolin-5-one (compound XXXV), or with N-methyl-2- $\{2-[\alpha-methyl-3-(trifluoromethyl)benzyloximinomethyl]phenyl\}-2-methoximinoacetamide (compound XXXVI),$ 

or with a (S)-valinamide of formula XXXVII)

wherein

R<sub>20</sub> is isopropyl, sec.-butyl or tert.-butyl, and

 $R_{21}$  is 4-chlorophenyl, 4-tolyl, 4- methoxyphenyl or  $\beta$ -naphthyl, preferably the compound isopropyl 2-methyl-1-[(1-p-tolylethyl)carbamoyl]-(S)-propylcarbamate (compound XXXVIIa); or with a (S)-valinamide of formula XXXVIII

$$R_{20,0} \xrightarrow{N} (S) \xrightarrow{H} S$$

wherein

R<sub>20</sub> is isopropyl, sec.-butyl or tert.-butyl,

R<sub>22</sub> is halogen, methyl or methoxy,

and n is 0, 1, or 2;

or with an azole of formula XXXIX

$$CI \qquad OH \qquad N \qquad (XXXIX)$$

$$CH_2 - C - CH_2 - N \qquad N \qquad S - R_{24}$$

wherein

R<sub>23</sub> is chloro or fluoro, and

R<sub>24</sub> is hydrogen or methyl;

is particularly effective in combating or preventing fungal diseases of crop plants. These combinations exhibit synergistic fungicidal activity.

Among the components b) all the compounds except those of formulae XXV to XXXIX are mentioned as a particular subgroup.

Throughout this document the expression combination stands for the various combinations of components a) and b), e.g. in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, e.g. a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, e.g. a few hours

or days. The order of applying the components a) and b) is not essential for working the present invention.

The combinations according to the invention may also comprise more than one of the active components b), if broadening of the spectrum of disease control is desired. For instance, it may be advantageous in the agricultural practice to combine two or three components b) with the any of the compounds of formula I, or with any preferred member of the group of compounds of formula I.

From WO 95/18789, WO 95/21154 and WO 97/20809 the following specific species of formula I are known:

Compound No.	R <sub>1</sub>	R₂
1.01	Н	4-CH <sub>3</sub>
1.02	Н	4-C <sub>2</sub> H <sub>5</sub>
1.03	2-Cl	4-CI
1.04	Н	4-CN
1.05	Н	4-OCF₃
1.06	2-F	4-CH <sub>3</sub>
1.07	2-F	4-F
1.08	2-CI	4-F
1.09	2-F	4-Cl
1.10	2-F	4-CF <sub>3</sub>

A preferred embodiment of the present invention is represented by those combinations which comprise as component a) a compound of the formula I wherein  $R_1$  is fluoro or chloro and  $R_2$  is methyl, trifluoromethyl, fluoro, chloro or bromo.

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Most preferred subgroups of formula I are those wherein  $R_1$  is fluoro or chloro and  $R_2$  is methyl, chloro or fluoro; or wherein  $R_1$  and  $R_2$  are independently fluoro or chloro; or wherein  $R_1$  is hydrogen, fluoro or chloro and  $R_2$  is methyl, fluoro or chloro, provided that  $R_2$  is methyl when  $R_1$  is hydrogen.

Among the mixtures of present invention most preference is given to the mixtures of compounds I.01, I.03, I.05, I.06, I.07, I.08 and I.09 with the compounds of component b), especially the commercially available products falling within the given ranges, i.e. the commercial products mentioned throughout this document. Particular preference is given to the combination of compound I.01 with any of the components b), and to the combination of compound I.07 with any of the components b).

Salts of the azole, amine and morpholine active ingredients are prepared by reaction with acids, e.g., hydrohalo acids such as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid, or sulfuric acid, phosphoric acid or nitric acid, or organic acids such as acetic acid, trifluoroacetic acid, trichloroacetic acid, propionic acid, glycolic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, formic acid, benzensulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, salicylic acid, p-aminosalicylic acid and 1,2-naphtalenedisulfonic acid.

The active ingredient combinations are effective against phytopathogenic fungi belonging to the following classes: Ascomycetes (e.g. Venturia, Podosphaera, Erysiphe, Monilinia, Mycosphaerella, Uncinula); Basidiomycetes (e.g. the genus Hemileia, Rhizoctonia, Puccinia); Fungi imperfecti (e.g. Botrytis, Helminthosporium, Rhynchosporium, Fusarium, Septoria, Cercospora, Alternaria, Pyricularia and Pseudocercosporella herpotrichoides); Oomycetes (e.g. Phytophthora, Peronospora, Bremia, Pythium, Plasmopara).

Target crops for the areas of indication disclosed herein comprise within the scope of this invention e.g. the following species of plants: cereals (wheat, barley, rye, oats, rice, sorghum and related crops); beet (sugar beet and fodder beet); pomes, stone fruit and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (marrows, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit

(oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocados, cinnamon, camphor); or plants such as maize, tobacco, nuts, coffee, sugar cane, tea, vines, hops, turf, bananas and natural rubber plants, as well as ornamentals (flowers, shrubs, broad-leaved trees and evergreens, such as conifers). This list does not represent any limitation.

The combinations of the present invention may also be used in the area of protecting technical material against attack of fungi. Technical areas include wood, paper, leather, constructions, cooling and heating systems, ventilation and air conditioning systems, and the like. The combinations according the present invention can prevent the disadvantageous effects such as decay, discoloration or mold.

The combinations according to the present invention are particularly effective against powdery mildews and rusts, pyrenophora, rhynchosporium and leptosphaeria fungi, in particular against pathogens of monocotyledonous plants such as cereals, including wheat and barley. They are furthermore particularly effective against downy mildew species, especially against plasmopara in vine.

The amount of combination of the invention to be applied, will depend on various factors such as the compound employed, the subject of the treatment (plant, soil, seed), the type of treatment (e.g. spraying, dusting, seed dressing), the purpose of the treatment (prophylactic or therapeutic), the type of fungi to be treated and the application time.

Particularly preferred mixing partners of the compounds of formula II are those in which R<sub>3</sub> is methyl or cyclopropyl. These compounds are commonly known as pyrimethanil and cyprodinil.

Particularly preferred mixing partners of the compounds of formula III are those in which  $R_4$  is CI,  $R_5$  and  $R_6$  are H,  $R_7$  is  $CH_3$  and  $R_8$  is cyclopropyl and A is the moiety (i) (commonly known as cyproconazole), those wherein  $R_4$  and  $R_5$  are CI,  $R_6$  and  $R_7$  are H,  $R_8$  is propyl and A is the moiety (i) (commonly known as hexaconazole); those in which  $R_4$  is 4-chlorophenoxy,  $R_5$  is CI,  $R_6$ ,  $R_7$  and  $R_8$  are H and  $H_8$  are  $H_8$  is ethyl and  $H_8$  are  $H_8$  is ethyl and  $H_8$  and  $H_8$  are  $H_8$  is ethyl and  $H_8$  are  $H_8$  is ethyl and  $H_8$  and  $H_8$  are  $H_8$  and  $H_8$  and  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  are  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  are  $H_8$  and  $H_8$  are  $H_8$  ar

are H, R<sub>8</sub> is propyl and A is the moiety (ii) (commonly known as propiconazole); those in which R<sub>4</sub> is Cl, R<sub>5</sub> is H, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are CH<sub>3</sub> and A is the moiety (iii) (commonly known as tebuconazole); those in which  $R_4$  is CI,  $R_5$  is H and A is the moiety (iv) (commonly known as triticonazole); those in which  $R_4$  is H,  $R_5$  is F,  $R_9$  is 4-fluorophenyl and A is the moiety (v) (commonly known as flutriafol); those in which R<sub>4</sub> is H, R<sub>5</sub> is CI, R<sub>9</sub> is 4-fluorophenyl and A is the moiety (vi) (commonly known as epoxiconazole); those in which R4 is Cl, R5 is H, R10 is phenyl and A is the moiety (vii) (commonly known as fenbuconazole), those in which R<sub>4</sub> and R<sub>5</sub> are Cl, and A is the moiety (viii) (commonly known as bromuconazole); those in which R<sub>4</sub> and R<sub>5</sub> are Cl, R<sub>11</sub> is propyl and A is the moiety (ix) (commonly known as penconazole); those in which R₄ and R₅ are Cl, R₁₁ is allyloxy and A is the moiety (ix) (commonly known as imazalil); and those in which R4 and R5 are Cl, R11 is 1,1,2,2tetrafluoroethoxymethyl and A is the moiety (ix) (commonly known as tetraconazole); those wherein R<sub>4</sub> is F, R<sub>5</sub> is H, R<sub>8</sub> is CH<sub>3</sub>, R<sub>9</sub> is 4-fluorophenyl, and A is the moiety (x) (commonly known as flusilazole); those in which R<sub>4</sub> is chloro, R<sub>5</sub> is hydrogen, R<sub>6</sub> and R<sub>7</sub> are methyl and A is the moiety (xi) (commonly known as metconazole); those wherein R<sub>4</sub> and R<sub>5</sub> are chloro, R<sub>6</sub> and R<sub>7</sub> are H, R<sub>8</sub> is t-butyl and A is the moiety (xii) (commonly known as diniconazole); those wherein R4 and R5 are chloro and A is the moiety (xiii) (commonly known as fluquinconazole); those wherein R<sub>4</sub> is chloro, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> are H, R<sub>8</sub> is n-butyl and A is the moiety (xiv) (commonly known as myclobutanil); and those wherein R₄ is chloro, R₅ is H, R₆, R<sub>7</sub> and R<sub>8</sub> are methyl and A is the moiety (xv) (commonly known as triadimenol).

Particularly preferred mixing partners of the compounds of formula IV are those wherein R<sub>12</sub> is cyclododecyl (commonly known as dodemorph), or C<sub>10-13</sub>alkyl (commonly known as tridemorph), or 3-(4-tert-butylphenyl)-2-methylpropyl (commonly known as fenpropimorph).

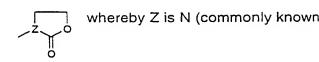
—Predominantly, the cis-positioning of the methyl groups at the morpholine ring is present in the compounds of formula IV when used in the combinations of the invention.

Particularly preferred mixing partners of the compounds of formula V are those wherein X and Y are O, and R<sub>13</sub> is 2-methylphenoxy-methyl (commonly known as kresoxim-methyl); or wherein X is NH, Y is N and R<sub>13</sub> is 2,5-dimethylphenoxy-methyl; or wherein X is O, Y is CH and R<sub>13</sub> is 4-(2-cyanophenoxy)-pyrimidin-6-yloxy (commonly known as azoxystrobin); or wherein X is O, Y is N and R<sub>13</sub> is 4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl (compound Va; proposed common name trifloxystrobin).

Particularly preferred mixing partners of the compounds of formula VI are those wherein R<sub>14</sub> and R<sub>15</sub> are both chloro (commonly known as fenpicionil); or wherein R14 and R15 together form a bridge -O-CF<sub>2</sub>-O- (commonly known as fludioxonil).

Particularly preferred mixing partners of the compounds of formula VII are those wherein  $R_{16}$  is benzyl and  $R_{17}$  is 1-methoxycarbonyl-ethyl (commonly known as benalaxyl); or wherein  $R_{16}$  is 2-furanyl and  $R_{17}$  is 1-methoxycarbonyl-ethyl (commonly known as furalaxyl); or wherein  $R_{16}$  is methoxymethyl and  $R_{17}$  is 1-methoxycarbonyl-ethyl or is (R)-1-methoxycarbonyl-ethyl (commonly known as metalaxyl and R-metalaxyl); or wherein  $R_{16}$  is chloromethyl and  $R_{17}$  is  $\frac{1}{2}$  whereby Z is CH (commonly known as orfurace);

or wherein  $R_{16}$  is methoxymethyl and  $R_{17}$  is



as oxadixyl).

Particularly preferred mixing partners of the compounds of formula VIII are those wherein  $R_{18}$  and  $R_{19}$  together form the bridge -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>- (commonly known as captan); or wherein  $R_{18}$  and  $R_{19}$  together form the bridge =CH-CH=CH-CH= (commonly known as folpet).

The compound of formula IX is commonly known as prochloraz.

The compound of formula X is commonly known as triflumizole.

The compound of formula XI is commonly known as pyrifenox.

The compound of formula XII is commonly known as acibenzolar-S-methyl.

The compound of formula XIII is commonly known as chlorothalonil.

The compound of formula XIV is commonly known as cymoxanil.

The compound of formula XV is commonly known as dimethomorph.

The compound of formula XVI is commonly known as famoxadone.

The compound of formula XVII is commonly known as fenhexamide.

The compound of formula XVIII is commonly known as fenarimol.

The compound of formula XIX is commonly known as fluazinam.

The compound of formula XX is commonly known as fosetyl-aluminium.

The compound of formula XXI is commonly known as quinoxyfen.

The compound of formula XXII is commonly known as fenpropidine.

The compound of formula XXIII is commonly known as spiroxamine.

The compound of formula XXIV is commonly known as carbendazime.

The compound of formula XXXV is commonly known as fenamidone.

The compound of formula XXXVIIa is commonly known as iprovalicarb (proposed common name).

The specific compounds b) mentioned in the preceding paragraphs are commercially available. Other compounds falling under the scope of the various groups of component b) are obtainable according to procedures analogous to those known for preparing the commercially available compounds.

It has been found that the use of compounds of formulae II to XXXVII in combination with the compound of formula I surprisingly and substantially enhance the effectiveness of the

latter against fungi, and vice versa. Additionally, the method of the invention is effective against a wider spectrum of such fungi that can be combated with the active ingredients of this method, when used solely.

Specific preferred mixtures according to the present invention are understood to be represented by the combinations of active ingredients of formula I, or any of the subgroups of formula I, or specifically mentioned members of the subgroups with a second fungicide selected from the group comprising pyrimethanil, cyprodinil, cyproconazole, hexaconazole; difenoconazole, etaconazole, propiconazole, tebuconazole, triticonazole, flutriafol, epoxiconazole, fenbuconazole, bromuconazole, penconazole, imazalil, tetraconazole, flusilazole, metconazole, diniconazole, fluquinconazole, myclobutanil, triadimenol, dodemorph, tridemorph, fenpropimorph, mancozeb, maneb, metiram, zineb, copper hydroxide, copper oxychloride, copper sulfate, oxine-copper, sulfur, kresoxim-methyl, azoxystrobin, 2-[2-(2,5-dimethylphenoxy-methyl)-phenyl]-2-methoximino-acetic acid N-methyl-amide, methyl 2-{2-[4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl]-phenyl}-2methoxyimino-acetate, fenpiclonil, fludioxonil, benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, orfurace, oxadixyl, captan, folpet, prochloraz, triflumizole, pyrifenox, acibenzolar-S-methyl, chlorothalonil, cymoxanil, dimethomorph, famoxadone, fenhexamide, fenarimol, fluazinam, fosetyl-aluminium, quinoxyfen, fenpropidine, spiroxamine, and carbendazime. Further preferred as second fungicide of component b) are fenamidone and iprovalicarb.

From this group a subgroup b1 is preferred comprising combinations with cyproconazole, hexaconazole; difenoconazole, propiconazole, tebuconazole, flutriafol, epoxiconazole, fenbuconazole, bromuconazole, penconazole, tetraconazole, flusilazole, metconazole, diniconazole, triadimenol, fluquinconazole and prochloraz.

From this group combinations with propiconazole, difenoconazole, penconazole, tebuconazole, prochloraz, epoxiconazole and cyproconazole are of particular interest as preferred embodiments of this invention as subgroup b1a.

A further preferred subgroup b2 comprises combinations with comprising cyprodinil, tridemorph, fenpropimorph, kresoxim-methyl, azoxystrobin, methyl 2-{2-[4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl]-phenyl}-2-methoxyimino-acetate,

acibenzolar-S-methyl, chlorothalonil, famoxadone, quinoxyfen, fenpropidine and carbendazime.

From this group combinations with cyprodinil, fenpropimorph, kresoxim-methyl, azoxystrobin, methyl 2-{2-[4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl]-phenyl}-2-methoxyimino-acetate, acibenzolar-S-methyl and fenpropidine are of particular interest as preferred embodiments of this invention as subgroup b2a.

Further groups of interest are the following combinations: compound I.01 with groups b1 and b2, or with groups b1a and b2a; compound I.03 with groups b1 and b2, or with groups b1a and b2a; compound I.05 with groups b1 and b2, or with groups b1a and b2a; compound I.06 with groups b1 and b2, or with groups b1a and b2a; compound I.07 with groups b1 and b2, or with groups b1a and b2a; compound I.08 with groups b1 and b2, or with groups b1a and b2a; compound I.09 with groups b1 and b2, or with groups b1a and b2a.

The weight ratio of a):b) is so selected as to give a synergistic fungicidal action. In general the weight ratio of a):b) is between 10:1 and 1:400. The synergistic action of the composition is apparent from the fact that the fungicidal action of the composition of a) + b) is greater than the sum of the fungicidal actions of a) and b).

Where the component b) is an anilinopyrimidine of formula II the weight ratio of a):b) is for example between 1:2 and 1:36, especially 1:2 and 1:18, and more preferably 1:3 and 1:8.

Where the component b) is an azole fungicide of formula III the weight ratio of a):b) is for example between 10:1 and 1:20, especially 5:1 and 1:10, and more preferably 2:1 and 1:4.

Where component b) is a morpholine fungicide of formula IV, the weight ratio of a): b) is for example between 1:2 and 1:30, especially 1:3 and 1:15, and more preferably 1:3 and 1:10.

Where component b) is a strobilurin fungicide of formula V, the weight ratio of a): b) is for example between 5:1 and 1:10, especially 3:1 and 1:3, and more preferably 1:2 and 1:5.

Where component b) is a pyrrole fungicide of formula VI, the weight ratio of a): b) is for example between 1:3 and 1:30, especially 1:1.5 and 1:7, and more preferably 1:2 and 1:5.

Where component b) is a phenylamide fungicide of formula VII, the weight ratio of a): b) is for example between 3:1 and 1:12, especially 2.5:1 and 1:6,. and more preferably 2:1 to 1:3.

Where component b) is a dithiocarbamte fungicide, the weight ratio of a): b) is for example between 1:3 and 1:120, especially 1:4 and 1:60, and more preferably 1:7 and 1:25.

Where component b) is a copper compound fungicide, the weight ratio of a): b) is for example between 1:1.5 and 1:100, especially 1:2 and 1:50, and more preferably 1:5 and 1:30.

Where component b) is a sulfur fungicide, the weight ratio of a): b) is for example between 1:6 and 1:400, especially 1:8 and 1:200, and more preferably 1:10 and 1:100.

Where component b) is a phthalimide fungicide of formula VIII, the weight ratio of a): b) is for example between 1:3 and 1:80, especially 1:4 and 1:40, and more preferably 1:8 and 1:20.

Where component b) is the compound of formula IX, the weight ratio of a): b) is for example between 1:2 and 1:25, especially 1:4 and 1:12, and more preferably 1:5 and 1:8.

Where component b) is the compound of formula X, the weight ratio of a): b) is for example between 3:1 and 1:16, especially 2.5:1 and 1:8, and more preferably 1:1 and 1:4.

Where component b) is the compound of formula XI, the weight ratio of a): b) is for example between 8:1 and 1:4, especially 2.5:1 and 1:2, and more preferably 2:1 and 1:1.

Where component b) is the compound of formula XII, the weight ratio of a): b) is for example between 6:1 and 1:2, especially 6:1 and 2:1, and more preferably 5:1 and 2:1.

Where component b) is the compound of formula XIII, the weight ratio of a): b) is for example between 1:3 and 1:40, especially 1:4 and 1:20, and more preferably 1:5 and 1:10.

Where component b) is the compound of formula XIV, the weight ratio of a): b) is for example between 3:1 and 1:8, especially 2.5:1 and 1:4, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XV, the weight ratio of a): b) is for example between 1.5:1 and 1:12, especially 1:1 and 1:6, and more preferably 1:1 and 1:4.

Where component b) is the compound of formula XVI, the weight ratio of a): b) is for example between 1.5:1 and 1:10, especially 1:1 and 1:5, and more preferably 1:1 and 1:3.

Where component b) is the compound of formula XVII, the weight ratio of a): b) is for example between 2:1 and 1:30, especially 1.5:1 and 1:15, and more preferably 1:1 and 1:5.

Where component b) is the compound of formula XVIII, the weight ratio of a): b) is for example between 8:1 and 1:4, especially 2.5:1 and 1:2, and more preferably 2:1 and 1:1.

Where component b) is the compound of formula XIX, the weight ratio of a): b) is for example between 1.5:1 and 1:12, especially 1:1 and 1:6, and more preferably 1:1 and 1:4.

Where component b) is the compound of formula XX, the weight ratio of a): b) is for example between 1:3 and 1:80, especially 1:4 and 1:40 and more preferably 1:1 and 1:25.

Where component b) is the compound of formula XXI, the weight ratio of a): b) is for example between 2:1 and 1:5, especially 1.5:1 and 1:2.5, and more preferably 1:1 and 1:2.

Where component b) is the compound of formula XXII, the weight ratio of a): b) is for example between 1:2 and 1:30, especially 1:3 and 1:15, and more preferably 1:3 and 1:10.

Where component b) is the compound of formula XXIII, the weight ratio of a): b) is for example between 1:2.5 and 1:30, especially 1:3 and 1:15, and more preferably 1:3 and 1:10.

Where component b) is the compound of formula XXIV, the weight ratio of a): b) is for example between 1.5:1 and 1:10, especially 1:1 and 1:5, and more preferably 1:2 and 1:4.

Where component b) is the compound of formula XXV, the weight ratio of a): b) is for example between 5:1 and 1:20, especially 2:1 and 1:20, and more preferably 1:1. and 1:10.

Where component b) is the compound of formula XXVI, the weight ratio of a): b) is for example between 5:1 and 1:20, especially 2:1 and 1:20, and more preferably 1:1 and 1:10.

Where component b) is the compound of formula XXVII, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XXVIII, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XXIX, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XXX, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XXXI, the weight ratio of a): b) is for example between 5:1 and 1:20, especially 2:1 and 1:10, and more preferably 1:1 and 1:5.

Where component b) is the compound of formula XXXII, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 2:1 and 1:2, and more preferably 1.5:1 and 1:1.5.

Where component b) is the compound of formula XXXIII, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XXXIV, the weight ratio of a): b) is for example between 5:1 and 1:20, especially 3:1 and 1:10, and more preferably 2:1 and 1:5. Where component b) is the compound of formula XXXV, the weight ratio of a): b) is for example between 6:1 and 1:6, especially 2:1 and 1:5, and more preferably 2:1 and 1:2.

Where component b) is the compound of formula XXXVI, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3 and more preferably 2:1. and 1:2.

Where component b) is a compound of formula XXXVII, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3 and more preferably 2:1. and 1:2.

Where component b) is a compound of formula XXXVIII, the weight ratio of a): b) is for example between 5:1 and 1:5, especially 3:1 and 1:3 and more preferably 2:1, and 1:2.

Where component b) is a compound of formula XXXIX, the weight ratio of a): b) is for example between 10:1 and 1:20, especially 5:1 and 1:10 and more preferably 2:1. and 1:4.

The method of the invention comprises applying to the treated plants or the locus thereof in admixture or separately, a fungicidally effective aggregate amount of a compound of formula I and a compound of component b).

The term locus as used herein is intended to embrace the fields on which the treated crop plants are growing, or where the seeds of cultivated plants are sown, or the place where the seed will be placed into the soil. The term seed is intended to embrace plant propagating material such as cuttings, seedlings, seeds, germinated or soaked seeds.

The novel combinations are extremely effective on a broad spectrum of phytopathogenic fungi, in particular from the Ascomycetes and Basidiomycetes classes. Some of them have a systemic action and can be used as foliar and soil fungicides.

The fungicidal combinations are of particular interest for controlling a large number of fungi in various crops or their seeds, especially wheat, rye, barley, oats, rice, maize, lawns, cotton, soybeans, coffee, sugarcane, fruit and ornamentals in horticulture and viticulture, in vegetables such as cucumbers, beans and cucurbits, and in field crops such as potatoes, tobacco and sugarbeets.

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The combinations are applied by treating the fungi or the seeds, plants or materials threatened by fungus attack, or the soil with a fungicidally effective amount of the active ingredients.

The agents may be applied before or after infection of the materials, plants or seeds by the fungi.

The novel combinations are particularly useful for controlling the following plant diseases:

Erysiphe graminis in cereals,

Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits,

Podosphaera leucotricha in apples,

Uncinula necator in vines,

Puccinia species in cereals,

Rhizoctonia species in cotton, rice and lawns,

Ustilago species in cereals and sugarcane,

Venturia inaequalis (scab) in apples,

Helminthosporium species in cereals,

Septoria nodorum in wheat,

Septoria tritici in wheat wheat,

Rhynchosporium secalis on barley,

Botrytis cinerea (gray mold) in strawberries, tomatoes and grapes,

Cercospora arachidicola in groundnuts,

Peronospora tabacina in tobacco,

Pseudocercosporella herpotrichoides in wheat and barley,

Pyrenophera teres in barley,

Pyricularia oryzae in rice,

Phytophthora infestans in potatoes and tomatoes,

Fusarium and Verticillium species in various plants,

Plasmopara viticola in grapes,

Alternaria species in fruit and vegetables.

When applied to the plants the compound of formula I is applied at a rate of 25 to 150 g/ha, particularly 50 to 125 g/ha, e.g. 75, 100, or 125g/ha, in association with 20 to 3000 g/ha, particularly 20 to 2000 g/ha, e.g. 20.g/ha, 30 g/ha, 40 g/ha, 75 g/ha, 80 g/ha, 100 g/ha, 125 g/ha, 150 g/ha, 175 g/ha, 200 g/ha, 300 g/ha, 500 g/ha, 1000 g/ha, 1200 g/ha, 1500 g/ha, 2000 g/ha, or in some cases like sulfur up to 10000 g/ha of a compound of component b), depending on the class of chemical employed as component b).

Where the component b) is an anilinopyrimidine of formula II for example 300 to 900 g a.i./ha is applied in association with the compound of formula I. Where the component b) is an azole fungicide of formula III for example 20 to 350 g a.i./ha is applied in association with the compound of formula I. Where the component b) is an morpholine of formula IV for example 300 to 750 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a strobilurin of formula V for example 75 to 250 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a pyrrole of formula VI for example 200 to 750 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a phenylamide of formula VII for example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a dithiocarbamate for example 500 to 3000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a copper compound for example 250 to 2500 g a.i. is applied in association with the compound of formula I. Where the component b) is sulfur for example 1000 to 10000 g a.i. is applied in association with the compound of formula I. Where the component b) is a phthalimide of formula VIII for example 500 to 2000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula IX for example 400 to 600 g a.i./ha is applied in association with the-compound of formula I. Where the component b) is the compound of formula X for example 50 to 400 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XI for example 20 to 100 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XII for example 20 to 40 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XIII for example 500 to 1000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XIV for example 50 to 200 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XV for example 100 to 300 g a.i./ha is applied in association with the compound of

formula I. Where the component b) is the compound of formula XVI for example 125 to 250 g a.i./ha is applied in association with the compound of formula 1. Where the component b) is the compound of formula XVII for example 100 to 750 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XVIII for example 20 to 100 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XIX for example 100 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XX for example 500 to 2000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXI for example 75 to 125 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXII for example 300 to 750 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXIII for example 375 to 750 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXIV for example 125 to 250 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXV for example 50 to 2000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXVI for example 50 to 2000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXVII for example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXVIII for example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXIX for example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXX for example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXXI for example 100 to 1000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXXII for example 50 to 200 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXXIII for example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXXIV for example 20 to 2000 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXXV for example 50 to 400 g a.i./ha is applied in association with the compound of formula I. Where the component b) is the compound of formula XXXVI for

example 50 to 300 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a compound of formula XXXVII for example 50 to 400 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a compound of formula XXXVIII for example 50 to 400 g a.i./ha is applied in association with the compound of formula I. Where the component b) is a compound of formula XXXIX for example 20 to 350 g a.i./ha is applied in association with the compound of formula I.

In agricultural practice the application rates of the combination depend on the type of effect desired, and range from 0.02 to 4 kg of active ingredient per hectare.

When the active ingredients are used for treating seed, rates of 0.001 to 50 g a.i. per kg, and preferably from 0.01 to 10g per kg of seed are generally sufficient.

The invention also provides fungicidal compositions comprising a compound of formula I and a compound of component b).

The composition of the invention may be employed in any conventional form, for example in the form of a twin pack, an instant granulate, a flowable formulation, an emulsion concentrate or a wettable powder in combination with agriculturally acceptable adjuvants. Such compositions may be produced in conventional manner, e.g. by mixing the active ingredients with appropriate adjuvants (diluents or solvents and optionally other formulating ingredients such as surfactants). Also conventional slow release formulations may be employed where long lasting efficacy is intended.

Particularly formulations to be applied in spraying forms such as water dispersible concentrates or wettable powders may contain surfactants such as wetting and dispersing agents, e.g. the condensation product of formaldehyde with naphthalene sulphonate, an alkylarylsulphonate, a lignin sulphonate, a fatty alkyl sulphate, and ethoxylated alkylphenol and an ethoxylated fatty alcohol.

A seed dressing formulation is applied in a manner known per se to the seeds employing the combination of the invention and a diluent in suitable seed dressing formulation form, e.g. as an aqueous suspension or in a dry powder form having good adherence to the seeds. Such seed dressing formulations are known in the art. Seed dressing formulations

may contain the single active ingredients or the combination of active ingredients in encapsulated form, e.g. as slow release capsules or microcapsules.

In general, the formulations include from 0.01 to 90% by weight of active agent, from 0 to 20% agriculturally acceptable surfactant and 10 to 99.99% solid or liquid adjuvant(s), the active agent consisting of at least the compound of formula I together with a compound of component b), and optionally other active agents, particularly microbides or conservatives or the like. Concentrated forms of compositions generally contain in between about 2 and 80%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight, preferably from 0.01 to 5% by weight of active agent. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations.

The Examples which follow serve to illustrate the invention, "active ingredient" denoting a mixture of compound I and a compound of component b) in a specific mixing ratio.

## Formulation Examples

Wettable powders	a)	b)	c)
active ingredient [I : comp b) = 1:3(a),	25 %	50 %	<b>75</b> %
1:2(b), 1:1(c)]			
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutyInaphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether	-	2 %	-
(7-8 mol of ethylene oxide)			
highly dispersed silicic acid	5 %	10 %	10 %
kaolin	62 %	27 %	-

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of the desired concentration.

Emuls	ifiable	concent	<u>trate</u>

active ingredient (I : comp b) = 1:6)	10 %
octylphenol polyethylene glycol ether	3 %
(4-5 mol of ethylene oxide)	
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
cyclohexanone	30 %
xylene mixture	50 %

Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

<u>Dusts</u>	a)	b)	c)
active ingredient [I : comp b) = 1:6(a),	5 %	6 %	4 %
1:2(b), 1:10(c)]			
talcum	95 %		-
kaolin	-	94 %	-
mineral filler	-	-	96 %

Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill. Such powders can also be used for dry dressings for seed.

# Extruder granules

active ingredient (I : comp b) = 2:1)	15 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
kaolin	82 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

#### Coated granules

active ingredient (I :comp b) = 1:10)	8 %
polyethylene glycol (mol. wt. 200)	3 %
kaolin	89 %

The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

#### Suspension concentrate

active ingredient (I : comp b) = 1:8)	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether	6 %
(15 mol of ethylene oxide)	
sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil (in the form of a 75 % emulsion in water)	1 %
water	32 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

### Slow Release Capsule Suspension

28 parts of a combination of the compound of formula I and a compound of component b), or of each of these compounds separately, are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of

- 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts
- 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed.

The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns.

The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

# **Biological Examples**

A synergistic effect exists whenever the action of an active ingredient combination is greater than the sum of the actions of the individual components.

The action to be expected E for a given active ingredient combination obeys the so-called COLBY formula and can be calculated as follows (COLBY, S.R. "Calculating synergistic and antagonistic responses of herbicide combination". Weeds, Vol. 15, pages 20-22; 1967): ppm = milligrams of active ingredient (= a.i.) per liter of spray mixture X = % action by active ingredient I using p ppm of active ingredient Y = % action by active ingredient II using q ppm of active ingredient.

According to COLBY, the expected (additive) action of active ingredients I+II using p+q ppm of active ingredient is  $E = X + Y - \frac{X \cdot Y}{100}$ 

If the action actually observed (O) is greater than the expected action (E), then the action of the combination is superadditive, i.e. there is a synergistic effect.

Alternatively the synergistic action may also be determined from the dose response curves according to the so-called WADLEY method. With this method the efficacy of the a.i. is determined by comparing the degree of fungal attack on treated plants with that on untreated, similarly inoculated and incubated check plants. Each a.i. is tested at 4 to 5 concentrations. The dose response curves are used to establish the EC90 (i.e. concentration of a.i. providing 90% disease control) of the single compounds as well as of the combinations (EC 90<sub>observed</sub>). The thus experimentally found values of the mixtures at a given weight ratio are compared with the values that would have been found were only a complementary efficacy of the components was present (EC 90 (A+B)<sub>expected</sub>). The

EC 90 (A+B)<sub>expected</sub> is calculated according to Wadley (Levi et al., EPPO- Bulletin <u>16</u>, 1986, 651-657):

wherein a and b are the weight ratios of the compounds A and B in the mixture and the indexes (A), (B), (A+B) refer to the observed EC 90 values of the compounds A, B or the given combination A+B thereof. The ratio EC90 (A+B)<sub>expected</sub> / EC90 (A+B)<sub>observed</sub> expresses the factor of interaction (F). In case of synergism, F is >1.

#### Example B-1: Action against Botrytis cinerea on apple fruits

Artificially damaged apples are treated by dropping a spray mixture of the active ingredient mixture onto the damage sites. The treated fruits are inoculated two hours later with a spore suspension of the fungus and incubated for six days at high humidity and 18°C. The fungicidal action of the test compound is derived from the radial growth of the fungus on treated fruits relative to untreated fruits.

# Example B-2: Efficacy against *Erysiphe graminis* f.sp. *tritici* on wheat a) Protective Treatment:

Fifteen wheat seeds c.v. "Arina" are sown in plastic pots of 50 ml and grown for 7 to 12 days at 22/19°C, 50-70% rH in the greenhouse. When the primary leaves have fully expanded, the plants are spray treated with aqueous spray liquids containing the single compounds, or mixtures thereof (hereinafter a.i.). All compounds are used as experimental or commercially available formulations, combinations are applied as tank mixtures. The application comprises foliar spraying to near runoff (three pots per treatment). 7 days after the application, the plants are inoculated in a settling tower with fresh spores of *Erysiphe graminis* f. sp. *tritici* by dusting the conidia on the test plants The plants are then incubated in a growth chamber at 20°C, 60% rH. Six days after inoculation, the percentage of infection on primary leaves is evaluated. The efficacy of the a.i. is determined by comparing the degree of fungal attack on treated plants with that on untreated, similarly inoculated and

incubated check plants. Each a.i. is tested at 3 to 5 concentrations. The results are evaluated according to the COLBY method.

# Results:

# aa) Mixtures of Compound 1.07 with Cyproconazole, E. graminis, protective

Comp. 1.07 (mg a.i./l)	Cyproconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.0025			2	
0.005			2	]
0.01			3	
0.025			20	
	0.01		3	
	0.025		5	
	0.05		7	
	0.1	,	12	
0.0025	0.01	1:4	17	6
	0.025	1:10	20	7
0.005	0.01	1:2	23	6
	0.025	1:5	. 38	7
	0.05	.1:10	42	9
0.01	0.01	1:1	17	6
İ	0.05	1:5	15	10
0.025	0.025	1:1	23	24
	0.05	1:2	42	26
	0.1	1:4	40	30

# ab) Mixtures of Compound 1.07 with Propiconazole, E. graminis. protective

Comp. 1.07 (mg a.i./l)	Propiconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.01			0	
0.025			3	
0.05			4	
0.1			7	
0.25			10	
	0.025		2	
	0.05		6	
	0.1		7	
	0.25		11	
	0.5		24	
0.01	0.01	1:1	6	0
	0.05	1:5	20	6
	0.1	1:10	27	7
0.025	0.025	1:1	10	5
	0.05	1:2	21	9
	0.1	1:4	33	10
	0.25	1:10	38	14

0.05	0.01	5:1	30	4
	0.025	2:1	25	6
	0.05	1:1	29	10
	0.1	1:2	30	11
	0.25	1:5	37	15
	0.5	1:10	42	27
0.1	0.025	4:1	23	9
	0.05	2:1	33	13
	0.1	1:1	34	14
1	0.5	1:5	34	29
	1	1:10	44	39
0.25	0.05	5:1	40	15
1	0.25	1:1	38	20
	0.5	1:2	44	32
	1	1:4	42	41

#### b) Curative Treatment:

Wheat plants cv. Arina are grown in standard soil in 50 ml pots (approx. 15 plants per pot) in the greenhouse at 22/19 °C and 14 hours light per day. At test begin the plants are 8 days old. For inoculation, conidia are dusted over the test plants and the plants are incubated at 18-20°C until treatment. The fungicide treatment is carried out 3 days after inoculation by spraying the test plants with diluted spray suspensions of the individual active ingredients or mixtures, being prepared by suspension in demineralized water and appropriate dilution.

12 plants in 3 pots are used for each treatment. 3 to 4 days after treatment the tests are evaluated by estimating the percentage of fungal attack on the leaves. The activity is calculated relative to the disease on the check plants. The fungicide interactions in the mixtures are calculated according to the COLBY method.

## Results:

ba) Mixtures of Compound 1.07 with Cyprodinil, E. graminis, curative

Comp. 1.07 (mg a.i./l)	Cyprodinil (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.25 0.5 1			43 47 54	
	0.25 0.5 2.5 5 10		0 0 0 0 0	

0.25	0.25	1:1	64	43
,	0.5	1:2	51	43
	2.5	1:10	63	44
0.5	0.5	1:1	58	47
	5	1:10	76	47
1	5	1:5	64	54
	10	1:10	70	54

# bb) Mixtures of Compound 1.07 with Cyproconazole, E. graminis, curative

Comp. 1.07 (mg a.i./l)	Cyproconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.0025 0.005 0.01 0.025			1 6 7 10	
	0.025 0.05 0.1		5 6 18	
0.0025	0.025	1:10	16	6
0.005	0.025 0.05	1:5 1:10	13 24	11 12
0.01	0.01 0.05	1:1 1:5	20 21	11 13
0.025	0.025 0.05 0.1	1:1 1:2 1:4	27 24 28	15 15 26

# bc) Mixtures of Compound 1.07 with Fenpropidin, E. graminis, curative (2 days)

	Comp. 1.07 (mg a.i./l)	Fenpropidin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
Т	0.5			41	
1	1			52	
- 1	2.5			72	·
Ī		0.5		8	
-1	· · · ·	1		8	
		2.5		13	
۱		· 5		27	
١		10		41	
t	0.5	0.5	1:1	59	46
ı	•	1	1:2	61	46
-		2.5	1:5	61 ·	· 49
١		5	1:10	68	57
Ì	1	1	1:1	87	.56
1		5	1:5	83	65
		10	1:10	83	71

2.5	2.5 5	1:1 1:2	89 90	76 80
	10	1:4	96	83
5	5	1:1	95	90
	10	1:2	95	90

### Example B-3: Activity against Uncinula necator

Grape plants in the 4-6 leaf stage, variety Gutedel, are inoculated with conidia of Uncinula necator by dusting the conidia over the test plants. After 2 days under high humidity and reduced light intensity, the plants are incubated for 10-14 days in a growth chamber at 70% rH and 22°C. 3 days after inoculation the active ingredients and the mixtures are applied by spraying aqueous suspensions being prepared by suspending the a.i.s in demineralized water and appropriate dilution. 5 plants are used for every treatment. 12 days after inoculation the tests are evaluated by estimating the percentage of fungal leaf attack relative to the disease on the check plants. The fungicide interactions in the mixtures are calculated according to COLBY method.

Results: Mixtures of Compound 1.07 with Penconazole, U. necator, curative

Comp. 1.07 (mg a.i./l)	Penconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.005 0.01 0.025 0.05			1 3 8 18	
	0.05 0.1		1 8	
0.005	0.05 0.05 0.1	1:10 1:5 1:10	16 16 32	4 11
0.025	0.05 0.1 0.25	1:2 1:4 1:10	31 41 13	9 15 23
0.05	0.05	1:1	26	19

# B-4: Activity against Puccinia recondita in wheat

#### Curative action

Wheat plants, cv. Arina are grown in standard soil in 4 cm square pots (approx. 15 plants per pot) in a climatic chamber at 18 °C and a photo period of 12 hours per day. At test begin the plants are 7 days old. A suspension of 80'000 conidia /ml (0.1% Tween 20) of Puccinia

recondita, is prepared from heavily sporulating cultures and sprayed on the test plants. The inoculated wheat plants are incubated in the green house for 24 hours under a plastic cover at 18-20°C and 100% rH with reduced light. Then they are incubated for further 7 days in the greenhouse at 18-20°C and 60 % rH and a photoperiod of 14 hours. After 48 hours the test plants were removed from the green house for treatment for the curative applications and returned back immediately there after. The active ingredients are suspended in water and diluted to the intended concentrations shortly prior to the application. For each application two replicates were made. The percentage of activity is estimated, relative to the disease attack on the inoculated check plants. The fungicide interactions in the mixtures are calculated according to the COLBY method.

### Results:

## a) Mixtures of Compound 1.07 with Cyproconazole, P. recondita, curative

Comp. 1.07 (mg a.i./l)	Cyproconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.01 0.025 0.05		-	0 0 0	
0.1			0	
0.25			0	
0.5			0	
1			0	
	0.05		15	
	0.1 0.25		5 65	
	0.25		65 90	
	0.5		85	
	2.5		98	
	5		95	
	10		100	
0.01	0.05	1:5	85	15
	0.1	1:10	90	5
0.025	0.05	1:2	90	15
	0.1	1:4	85	5
	0.25	1:10	90	65
0.05	0.05	1:1	80	15
	0.1	1:2	70 20	5
	0.25 0.5	1:5 1:10	90 95	65 00
0.1	0.05	2:1	80	90
0.1	0.05	1:1	75	15 5
	0.1	1:5	73 98	90
	1 1	1:10	98	85

0.05	5:1	0	15
		85	65
			90
1 1		98	85
2.5	1:10	95	98
		85	5
		80	65
		90	90
1			85
25			98
		98	95
		95	65
			90
1 1			85
5		100	95
	1:10	95	100
	0.05 0.25 0.5 1 2.5 0.1 0.25 0.5 1 2.5 5 0.25 0.5 1 5 1	0.25     1:1       0.5     1:2       1     1:4       2.5     1:10       0.1     5:1       0.25     2:1       0.5     1:1       1     1:2       2.5     1:5       5     1:10       0.25     4:1       0.5     2:1       1     1:1       5     1:5	0.25     1:1     85       0.5     1:2     90       1     1:4     98       2.5     1:10     95       0.1     5:1     85       0.25     2:1     80       0.5     1:1     90       1     1:2     98       2.5     1:5     100       5     1:10     98       0.25     4:1     95       0.5     2:1     95       1     1:1     98       5     1:5     100

# b) Mixtures of Compound 1.07 with Fenpropidin, P. recondita, curative

Comp. 1.07 (mg a.i./l)	Fenpropidine (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
5			35	
	1 2.5 5 10		0 0 0 0	
5	25 1 2.5 5 10 25	5:1 2:1 1:1 1:2 1:5	0 75 60 55 35 45	35 35 35 35 35

# c) Mixtures of Compound 1.07 with Propiconazole, P. recondita, curative

Comp. 1.07 (mg-a.i./l)-	Propiconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.25 0.5 1 2.5 5			0 0 0 30 35	
	1 2.5		0 20	
0.25	1 2.5	1 : 4 1 : 10	8 25	0 20
0.5	1 2.5	1:2 1:5	0 95	0 20

1	1	1:1	45	0
2.5	2.5	1:1	65	44
5	1	5:1	75	35
	2.5	2:1	85	48

## d) Mixtures of Compound 1.07 with Trifloxystrobin, P. recondita, curative

Comp. 1.07 (mg a.i./l)	Trifloxystrobin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
2.5 5			30 35	
	1 5 10 25 50		0 0 0 35 35	
2.5	5 25	1:2 1:10	50 75	30 55
5	1 5 10 25 50	5:1 1:1 1:2 1:5 1:10	65 70 75 75 80	35 35 35 58 58

## Example B-5: Activity against Phytophthora infestans in tomatoes

#### a) Curative action

Tomato plants cv. "Roter Gnom" are grown for three weeks and then sprayed with a zoospore suspension of the fungus and incubated in a cabin at 18 to 20°C and saturated atmospheric humidity. The humidification is interrupted after 24 hours. After the plants have dried, they are sprayed with a mixture which comprises the active ingredient formulated as a wettable powder at a concentration of 200 ppm. After the spray coating has dried, the plants are returned to the humid chamber for 4 days. Number and size of the typical foliar lesions which have appeared after this time are used as a scale for assessing the efficacy of the test substances.

### b) Preventive-systemic action

The active ingredient which is formulated as a wettable powder is introduced, at a concentration of 60 ppm (relative to the soil volume), onto the soil surface of three-week-old tomato plants cv. "Roter Gnom" in pots. After an interval of three days, the underside of the leaves is sprayed with a zoospore suspension of Phytophthora infestans. They are then kept for 5 days in a spray cabinet at 18 to 20°C and saturated atmospheric humidity. After

this time, typical foliar lesions appear whose number and size are used for assessing the efficacy of the test substances.

# Example B-6: Activity against Septoria nodorum in wheat

## a) Protective action

Wheat plants, cv. Arina are grown in standard soil in 6.5 cm round pots (approx. 8 -10 plants per pot) in a climatic chamber at 18°C and a photo period of 12 hours per day. At begin of the test the plants are 7 days old. The plants are sprayed with a spray mixture of the active ingredients prepared shortly before application. After 8 days, the treated plants are infected with a conidia suspension of *Septoria nodorum* (700'000 conidia /ml; 0.02% Tween 20) prepared from heavily sporulating cultures. The inoculated wheat plants are incubated in the green house for 24 hours under a dark nylon cover at 22-24°C and 100% rH with reduced light. Then they are incubated for further 5 days in the greenhouse at 22-24°C and 65 % rH and a photoperiod of 14 hours. For each application two replicates are made. The percentage of activity is estimated, relative to the disease attack on the inoculated check plants. The fungicide interactions in the mixtures are calculated according to the COLBY method.

## Results:

aa) Mixtures of Compound 1.07 with Cyproconazole, S. nodorum, preventive

uu, mmuu				
Comp. 1.07 (mg a.i./l)	Cyproconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.1			0	İ
0.5			0	
1			0	
2.5			75	
dila	0.1		0	
	0.5		0	<b>}</b>
	1		0	
	5	3	18	
Į.	10	'	35	
1	25		18	
0.1	0.1	1:1	35	0
	0.5	1:5	35	0
	1	1:10	50	0
0.5	0.1	5:1	65	0
0.0	5	1:10	65	18
	0.25	4:1	65	0
1	5	1:5	65	18
1	10	1:10	50	35

2.5	2.5	1:1	90	75
	5	1:2	95	79
	10	1:4	90	84
	25	1:10	98	79

# ab) Mixtures of Compound 1.07 with Cyprodinil, S. nodorum, preventive

Comp. 1.07 (mg a.i./l)	Cyprodinil (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.01 0.025			0	
0.025			Ö	
0.1			Ö	
0.5			0	·
1			0	
2.5	_		75	
	0.1		0	
	0.25		0	
	0.5		0	
	1		0	
	2.5		0	
0.04	10	1.10	65	0
0.01	0.1	1:10		
0.025	0.05	1:2	35 10	0
	0.1	1:4	18	0
0.25	1	1:4	18	0
0.5	11	1:2	35	0
	2.5	1:5	0	0
1	0.25	4:1	75	0
	0.5	2:1	70 25	0
	10	1:10	65	0
2.5	0.5	5:1	90	75
	2.5	1:1	90	75 75
	10	1:4	95	75

# ac) Mixtures of Compound 1.07 with Fenpropidin, S. nodorum, preventive

Comp. 1.07 (mg a.i./l)	Fenpropidin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.25			0	
1			0	]
2.5			75	
	0.05		0	ì
	0.25		0	İ
	0.5		0	
	1	Į į	18	
	2.5		0	
	5		0	[
	10		0	1
	25		0	

0.25	0.05	5:1	90	0
	0.25	1:1	90	0
	0.5	1:2	50	0
	1	1:4	50	18
1	0.25	4:1	50	0
	0.5	2:1	80	0
	1	1:1	75	18
	5	1:5	75	0
	10	1:10	75	0
2.5	0.5	5:1	90	75
	2.5	1:1	85	75
	5	1:2	80	<b>7</b> 5
	10	1:4	95	75
1	25	1:10	98	75

### b) Curative action

Wheat plants, cv. Arina are grown in standard soil in 4 cm square pots (approx. 15 plants per pot) in a climatic chamber at 18 °C and a photo period of 12 hours per day. At test begin the plants are 7 days old. A suspension of 700'000 conidia /ml (0.02% Tween 20) of Septoria nodorum, is prepared from heavily sporulating cultures and sprayed on the test plants. The inoculated wheat plants are incubated in the green house for 24 hours under a dark nylon cover at 22-24°C and 100% rH with reduced light. Then they are incubated for further 5 days in the greenhouse at 22-24°C and 65 % rH and a photoperiod of 14 hours. After 48 hours the test plants were removed from the green house for treatment for the curative applications and returned back immediately there after. The active ingredients are suspended in water and diluted to the intended concentrations shortly prior to the application. For each application two replicates are made. The percentage of activity is estimated, relative to the disease attack on the inoculated check plants. The fungicide interactions in the mixtures are calculated according to the COLBY method.

#### Results:

ba) Mixtures of Compound 1.07 with Fenpropidin, S. nodorum, curative

Comp. 1.07 (mg a.i./l)	Fenpropidin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.01 0.025 0.05			0 25 20	
	0.1 0.25 0.5		0 0 0	

0.01	0.1	1:10	35	0
0.025	0.1	1:4	90	25
	0.25	1:10	75	25
0.05	0.1	1:2	80	20
	0.25	1:5	55	20
	0.5	1:10	70	20

## bb) Mixtures of Compound 1.07 with Trifloxystrobin, S. nodorum, curative

Comp. 1.07 (mg a.i./l)	Trifloxystrobin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.01 0.025 0.05			0 25 20	
	0.05 0.1 0.25		0 0 18	
0.01	0.05	1:5	70	0
	0.1	1:10	75	0
0.025	0.05	1:2	80	25
	0.1	1:4	35	25
0.05	0.05	1:1	90	20
	0.1	1:2	95	20
	0.25	1:5	65	34
	0.5	1:10	65	60

### Example B-7: Activity against Phytophthora in potato plants

### a) Residual-protective action

2-3 week old potato plants (Bintje variety) are grown for 3 weeks and then sprayed with a spray mixture (0.02% of active ingredient) prepared with a wettable powder of the active ingredient. After 24 hours, the treated plants are infected with a sporangia suspension of the fungus. The fungus infestation is assessed after the infected plants have been incubated for 5 days at a relative atmospheric humidity of 90-100% and 20°C.

### b) Systemic action

A spray mixture (0.002% of active ingredient based on the soil volume) prepared with a wettable powder of the active ingredient is poured next to 2-3 week old potato plants (Bintje variety) which have been grown for 3 weeks. Care is taken that the spray mixture does not come into contact with the aerial parts of the plants. After 48 hours, the treated plants are infected with a sporangia suspension of the fungus. Fungus infestation is assessed after

the infected plants have been incubated for 5 days at a relative atmospheric humidity of 90-100% and 20°C.

# Example B-8: Activity against Phytophthora infestans in potatoes

Potatoes, cv. Bintje are cultivated under greenhouse conditions at 24/20°C in standard soil for 6 weeks. Leaf discs with a diameter of 10 mm are cut out of the leaves with the exception of the youngest and the oldest leaf. The leaf segments are placed with the upper leaf side down in petri dishes (Ø 5 cm), each containing 6 ml of 0.16 % water agar. The fungicides and mixtures are suspended in demineralized water and diluted appropriately. The fungicide treatment is carried out 1 day prior to inoculation. A total volume of 450 µl is applied on 6 leaf discs with an air brush. Freshly formed sporangia of *Phytophthora infestans* are harvested from infected potato slices and a sporangia suspension of 20'000 sporangia/ml is prepared; the suspension is incubated at 4°C for 15 min.. For inoculation, a drop of 30 µl is applied to each leaf disc. The leaf discs are incubated for 6 d at 18°C and a light period of 16 h until evaluation.

Six discs per treatment are evaluated. After the incubation period, the percentage of leaf attack is estimated and the activity is calculated relative to the check plants. The fungicide interactions in the mixtures are calculated according to the COLBY method.

Results:

Mixtures of Compound 1.07 with Trifloxystrobin

Comp. 1.07 (mg a.i./l)	Trifloxystrobin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.25 0.1			4 0	
	2.5 1 0.5 0.25 0.1		44 6 6 0 2	
0.25	2.5 1 0.5 0.25	1:10 1:4 1:2 1:1	67 59 9 17	46 10 9 4
0.1	1 0.5 0.25 0.1	1:10 1:5 1:2.5 1:1	20 19 20 15	6 6 0 2

## Example B-9: Activity against Helminthosporium teres on barley

Barley plants, cv. Express are grown in standard soil in 6.5 cm round pots (approx. 8-10 plants per pot) in a climatic chamber at 18 °C and at a photo period of 12 hours per day. At test begin the plants were 7 days old. The plants are sprayed with a spray mixture of the active ingredients prepared shortly before application. After 9 days, the treated plants are infected with a conidia suspension of *Helminthosporium teres* prepared from heavily sporulating cultures. A suspension of 30'000 conidia /ml (0.1% Tween 20) is prepared from the in-vitro cultures and sprayed immediately on the test plants. The inoculated barley plants are incubated in the green house for 3 days under a plastic cover at 20-22°C and 100% rH and a photoperiod of 14 hours. For each application two repetitions are made. The efficacy of the test combinations and the single active ingredients in this test is determined by comparing the degree of fungal attack with that on untreated, similarly inoculated check plants. The percentage of activity is estimated, relative to the disease attack on the inoculated check plants. The fungicide interactions in the mixtures are calculated according to the COLBY method.

#### Results:

## a) Mixtures of Compound 1.07 with Cyprodinil, H. teres, preventive

Comp. 1.07 (mg a.i./l)	Cyprodinil (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
2.5 5 10			35 50 60	
	10 25 50 100		0 0 0 0	
2.5	10	1:4	60	35
5	10 25 50	1:2 1:5 1:10	65 60 65	50 50 50
10	50 100	1:5 1:10	70 75	60 60

## b) Mixtures of Compound 1.07 with Fenpropidin, H. teres, preventive

	Comp. 1.07 (mg a.i./l)	Fenpropidin (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
Г	1			0	
	2.5			35	
	5			50	
L	10			60	

	0.25 0.5 2.5 5 10 25 50 100	4:1	0 0 0 0 0 0 0	0
1	0.25 5 10	1 : 5 1 : 10	35 20	0 0
2.5	0.5	5:1	45	35
	2.5	1:1	40	35
	10	1:4	50	35
	25	1:10	55	35
5	2.5	2:1	60	50
	5	1:1	50	50
	10	1:2	60	50
	25	1:5	55	50
	50	1:10	60	50
10	2.5	4:1	70	60
	5	2:1	70	60
	10	1:1	90	60
	50	1:5	80	60
	100	1:10	70	60

# c) Mixtures of Compound 1.07 with Propiconazole, H. teres, preventive

Comp. 1.07 (mg a.i./l)	Propiconazole (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
5 10			50 60	
	5 10 25 50		0 0 0 0	
5	5 10 25 50	1:1 1:2 1:5 1:10	55 65 70 80	50 50 50 50
10	10 50 100	1:1 1:5 1:10	55 75 80	60 60 67

# Example B-10: Action against Colletotrichum lagenarium on Cucumis sativus

a) After a cultivation period of 1 weeks, cucumber plants are sprayed with a spray mixture prepared from a wettable powder formulation of the test compounds (three concentrations each). After 96 hours, the plants are infected with a spore suspension (1.0 x 10<sup>5</sup> spores/ml)

of the fungus and incubated for 30 hours at high humidity and a temperature of 20°C. Incubation is then continued at normal humidity and 22°C to 23°C.

Evaluation of protective action is made 7 to 8 days after infection and is based on fungus infestation, relative to untreated check plants. The evaluation of the interaction of the two active ingredient components is calculated according to the COLBY method.

Results:

Mixtures of Compound 1.07 with Acibenzolar-S-methyl

Comp. 1.07 (mg a.i./l)	Acibenzolar-S- methyl (mg a.i./l)	Mixing ratio	% activity observed	% activity expected
0.06			0	
0.2			0	[
0.6			0	
	0.06		0	
	0.2		0	·
	0.6		0	
0.06	0.06	1:1	38	0
	0.2	1:3	75	0 [
	0.6	1:10	94	0
0.2	0.06	3:1	88	0
	0.2	1:1	<b>69</b> .	0
	0.6	1:3	88	0
0.6	0.06	10 : 1	93	0
	0.2	3:1	89	0
	0.6	1:1	94	0

b) After a cultivation period of 2 weeks, cucumber plants are treated by soil application with a spray mixture prepared from a wettable powder formulation of the test compound (concentration: 60 ppm, based on the volume of the soil). After 96 hours, the plants are infected with a spore suspension (1.5 x 10<sup>5</sup> spores/ml) of the fungus and incubated for 30 hours at high humidity and a temperature of 20°C. Incubation is then continued at normal humidity and 22°C.

Evaluation of protective action is made 7 to 8 days after infection and is based on fungus infestation.

The mixtures according to the invention exhibit good activity in the above Examples.

## WHAT IS CLAIMED IS:

- A method of combating phytopathogenic diseases on crop plants which comprises applying to the crop plants or the locus thereof being infested with said phytopathogenic disease an effective amount of a combination of
- a) a 2-(5-phenyl-3,6-diaza-2,7-dioxa-octa-3,5-dienyl)-phenylacrylamide of formula I

$$C = N - O - CH_3$$

$$C = N - O - CH_3$$

$$CH_2 - O - N = C - C = N - O - CH_3$$

$$CH_3$$

$$CH_3$$

$$C = N - O - CH_3$$

$$CH_3$$

$$CH_3$$

wherein

R<sub>1</sub> is hydrogen, fluoro or chloro,

R₂ is methyl, ethyl, trifluoromethyl, trifluoromethoxy, cyano, fluoro, chloro or bromo, with the proviso that R₂ cannot be fluoro, chloro or bromo, when R₁ is hydrogen; in association with

b) either an anilinopyrimidine of formula II

wherein

R<sub>3</sub> is methyl, 1-propynyl or cyclopropyl;

or an azole of formula III

$$R_{4} \longrightarrow A \longrightarrow N \longrightarrow N$$

$$R_{5} \longrightarrow N$$

$$(III)$$

wherein

A is selected from

(i) 
$$\frac{OH}{C-CH_2}$$
, (ii)  $\frac{C}{\beta}$   $CR_6R_7R_8$ 

(ii) 
$$\beta$$
  $O$   $CH_2$   $CR_6R_7R_8$ 

(iv) 
$$\xrightarrow{\beta}$$
  $\xrightarrow{OH}$   $\xrightarrow{OH}$   $\xrightarrow{CH_2}$   $\xrightarrow{R_7}$   $\xrightarrow{R_6}$ 

(v) 
$$\frac{OH}{A}$$
  $C - CH_2$  , (vi)  $R_9$ 

(v) 
$$\frac{OH}{\beta} \stackrel{C}{\underset{R_9}{\mid}} CH_2$$
, (vi)  $\frac{C}{\beta} \stackrel{C}{\underset{R_9}{\mid}} CH_2$ .

(viii) 
$$\beta$$
  $O$   $Br$ 

(ix) 
$$\frac{CH - CH_{2}}{\beta}$$
,

$$(x) \qquad \frac{R_{8}}{|}$$

$$\beta \qquad |$$

$$R_{9}$$

$$(xi) \qquad \begin{array}{c} -CH_2 \\ \beta \end{array} \qquad \begin{array}{c} OH \\ -CH_2 \\ \hline \\ R_7 \end{array} \qquad \begin{array}{c} (xii) \\ \hline \\ CR_6R_7R_8 \end{array} \qquad \begin{array}{c} CH \\ -CH_6R_7R_8 \end{array} \qquad .$$

(xii) 
$$\frac{}{\beta}$$
 CH  $\frac{}{}$  C $\frac{}{}$  CR<sub>6</sub>R<sub>7</sub>R<sub>8</sub>

(xiii) 
$$\beta$$
  $O = N$  ,  $(xiv)$   $\beta$   $C = CH_2$  and  $CR_6R_7R_8$  ;  $CH = OH$  ;  $CH = OH$   $CR_6R_7R_8$ 

whereby the  $\beta$ -carbon attaches to benzene ring of formula III, and wherein

R<sub>4</sub> is H, F, Cl, 4-fluorophenoxy or 4-chlorophenoxy;

R<sub>5</sub> is H, Cl or F;

R<sub>6</sub> and R<sub>7</sub> are independently H or CH<sub>3</sub>;

R<sub>8</sub> is C<sub>1-4</sub>alkyl or cyclopropyl;

R<sub>9</sub> is 4-chlorophenyl or 4-fluorophenyl;

R<sub>10</sub> is phenyl, and

 $R_{11}$  is allyloxy,  $C_{1-4}$ alkyl, or 1,1,2,2-tetrafluoroethoxy-methyl, and the salts of such azole fungicide;

or a morpholine fungicide of formula IV

$$H_3C$$

$$O$$

$$N-R_{12}$$

$$H_3C$$
(IV)

wherein

R<sub>12</sub> is C<sub>8-15</sub>cycloalkyl, C<sub>8-15</sub>alkyl, or C<sub>1-4</sub>alkylphenyl-C<sub>1-4</sub>alkyl,

and the salts of such morpholine fungicide;

or a strobilurin compound of formula V

$$Y-O-CH_3$$
 $CO-X-CH_3$ 
 $(V)$ 

wherein

X is NH or O,

Y is CH or N, and

 $R_{13}$  is 2-methylphenoxy-methyl, 2,5-dimethylphenoxy-methyl, 4-(2-cyanophenoxy)-pyrimidin-6-yloxy, or 4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl;

or a pyrrole compound of the formula VI

wherein

 $R_{14}$  and  $R_{15}$  are indendently halo, or together from a perhalomethylendioxo bridge; or a phenylamide of the formula VII

$$CH_3$$
  $CO-R_{16}$   $CH_3$   $CH_3$   $CH_3$ 

wherein

R<sub>16</sub> is benzyl, methoxymethyl, 2-furanyl or chloromethyl,

 $R_{17}$  is 1-methoxycarbonyl-ethyl, or

Z is CH or N;

or a dithiocarbamate fungicide selected from mancozeb, maneb, metiram and zineb; or a copper compound selected from copper hydroxide, copper oxychloride, copper sulfate and oxine-copper;

or sulfur;

or a phthalimide compound of the formula VIII

$$R_{18}$$
  $O$   $N-S-CCI_3$   $(VIII)$ 

wherein

 $R_{18}$  and  $R_{19}$  together form a 4-membered bridge -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>- or =CH-CH=CH-CH= ;

or with the compound of formula IX

$$CI \longrightarrow CI \longrightarrow CH_2-CH_2-N-CO-N \longrightarrow N$$
(IX);

or with the compound of formula X

$$CF_3 \qquad CH_2-O-C_3H_7-n$$

$$N=C \qquad N$$

$$N = C \qquad N$$

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$$N = C$$

or with the compound of formula XI

$$CI \longrightarrow C \longrightarrow CH_2 \longrightarrow N$$
 $N \longrightarrow CH_3$ 
 $(XI)$ 

or with the compound of formula XII

or with the compound of formula XIII

or with the compound of formula XIV

or with the compound of formula XV

$$C = CH - CO - N O$$

$$C = CH - CO - N O$$

$$C = CH - CO - N O$$

$$C = CH - CO - N O$$

$$C = CH - CO - N O$$

$$C = CH - CO - N O$$

$$C = CH - CO - N O$$

or with the compound of formula XVI

or with the compound of formula XVII

or with the compound of formula XVIII

or with the compound of formula XIX

$$F_3C$$
 $N$ 
 $N$ 
 $CI$ 
 $NO_2$ 
 $CI$ 
 $NO_2$ 
 $CI$ 
 $NO_2$ 
 $CI$ 
 $NO_2$ 
 $CI$ 
 $NO_2$ 
 $CI$ 
 $NO_2$ 
 $CI$ 

or with the compound of formula XX

$$\begin{bmatrix} O \\ H_3C - CH_2 - P - OH \\ H \end{bmatrix}_3 AI$$
 (XX)

or with the compound of formula XXI

or with the compound of formula XXII

$$\begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{2} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \hline \end{array} \begin{array}{c} CH_{3} \\ CH_{3$$

or with the compound of formula XXIII

$$H_3C \xrightarrow{CH_3} O \xrightarrow{CH_3} CH_3$$
 (XXIII) ;

or with the compound of formula XXIV

or with 2-chloro- N-(4'-fluoro-1,1'-biphenyl-2-yl)nicotinamide (compound XXV), or with 2-chloro- N-(4'-chloro-1,1'-biphenyl-2-yl)nicotinamide (compound XXVI), or with methyl N-(2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]phenyl)-N- methoxycarbamate (compound XXVII),

or with methyl N-(2-[1-(4-tolyl)pyrazol-3-yloxymethyl]phenyl)-N- methoxycarbamate (compound XXVIII),

or with 2-[4-methoxy-3-(1-methylethoxy)-1,4-diazabuta-1,3-dienyloxymethyl]phenyl-2-methoximino-N-methylacetamide (compound XXIX),

or with 2-[4-methoxy-3-(1-methylpropoxy)-1,4-diazabuta-1,3-dienyloxymethyl]phenyl-2-methoximino-N-methylacetamide (compound XXX),

or with N-(cyclopropylmethoxy)-N'-(2-phenylacetyl)-2,3-difluoro-6-trifluoromethylbenzamidine (compound XXXI),

or with N-[3'-(1'-chloro-3-methyl 2'-oxopentan)]-3,5-dichloro-4-methylbenzamide (compound XXXII),

or with methyl(2)-2-{6-[6-(trifluoromethyl)pyrid-2-yloxymethyl]-phenyl}-3-methoxyacrylate (compound XXXIII),

or with 2-chloro-4-(2-fluoro-2-methylpropionylamino)-N,N-dimethylbenzamide (compound XXXIV),

or with (S)-1-anilino-4-methyl-2-methylthio-4-phenylimidazolin-5-one (compound XXXV), or with N-methyl-2-{2-[α-methyl-3-(trifluoromethyl)benzyloximinomethyl]phenyl}-2-methoximinoacetamide (compound XXXVI), or with a (S)-valinamide of formula XXXVII)

$$R_{20.0}$$
  $N$   $(S)$   $R_{21}$   $R_{21}$ 

#### wherein

R<sub>20</sub> is isopropyl, sec.-butyl or tert.-butyl, and

R<sub>21</sub> is 4-chlorophenyl, 4-tolyl, 4- methoxyphenyl or β-naphthyl, preferably the compound isopropyl 2-methyl-1-[(1-p-tolylethyl)carbamoyl]-(S)-propylcarbamate (compound XXXVIIa), or with a (S)-valinamide of formula XXXVIII

### wherein

R<sub>20</sub> is isopropyl, sec.-butyl or tert.-butyl, R<sub>22</sub> is halogen, methyl or methoxy, and n is 0, 1, or 2; or with an azole of formula XXXIX

$$CI \qquad OH \qquad N \qquad (XXXIX)$$

$$CH_2 - C - CH_2 - N \qquad N \qquad S - R_{24}$$

wherein

R<sub>23</sub> is chloro or fluoro, and R<sub>24</sub> is hydrogen or methyl.

- 2. A method according to claim 1 wherein component b) does not comprise the compounds of formulae XXV to XXXVIII.
- 3. A method according to claim 1 wherein the component a) comprises a compound of the formula I wherein  $R_1$  is fluoro or chloro and  $R_2$  is methyl, trifluoromethyl, fluoro, chloro or bromo, or wherein  $R_1$  is fluoro or chloro and  $R_2$  is methyl, chloro or fluoro, or wherein  $R_1$  and  $R_2$  are independently fluoro or chloro, or wherein  $R_1$  is hydrogen, fluoro or chloro and  $R_2$  is methyl, fluoro or chloro, provided that  $R_2$  is methyl when  $R_1$  is hydrogen.
- 4. A method according to any one of claims 1 to 3 wherein the component b) is selected from the group comprising pyrimethanil, cyprodinil, cyproconazole, hexaconazole; difenoconazole, etaconazole, propiconazole, tebuconazole, triticonazole, flutriafol, epoxiconazole, fenbuconazole, bromuconazole, penconazole, imazalil, tetraconazole, flusilazole, metconazole, diniconazole, fluquinconazole, myclobutanil, triadimenol, dodemorph, tridemorph, fenpropimorph, mancozeb, maneb, metiram, zineb, copper hydroxide, copper oxychloride, copper sulfate, oxine-copper, sulfur, kresoxim-methyl, azoxystrobin, 2-[2-(2,5-dimethoxyphenoxy-methyl)-phenyl]-2-methoximino-acetic acid N-methyl-amide, methyl 2-{2-[4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl]-phenyl}-2-methoxyimino-acetate, fenpiclonil, fludioxonil, benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, orfurace, oxadixyl, captan, folpet, prochloraz, triflumizole, pyrifenox, acibenzolar-S-methyl, chlorothalonil, cymoxanil, dimethomorph, famoxadone, fenhexamide, fenarimol, fluazinam, fosetyl-aluminium, quinoxyfen, fenpropidine, spiroxamine, and carbendazime.

- 5. A method according to any one of calims 1 to 3 wherein the component b) is fenamidone or iprovalicarb.
- 6. A method according to claim 4 wherein component b) is selected from a group comprising cyproconazole, hexaconazole; difenoconazole, propiconazole, tebuconazole, flutriafol, epoxiconazole, fenbuconazole, bromuconazole, penconazole, tetraconazole, flusilazole, metconazole, diniconazole, triadimenol, fluquinconazole and prochloraz; and especially propiconazole, difenoconazole, penconazole, tebuconazole, prochloraz, epoxiconazole and cyproconazole.
- 7. A method according to claim 4 wherein component b) is selected from a group comprising cyprodinil, tridemorph, fenpropimorph, kresoxim-methyl, azoxystrobin, methyl 2-{2-[4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl]-phenyl}-2-methoxyimino-acetate, acibenzolar-S-methyl, chlorothalonil, famoxadone, quinoxyfen, fenpropidine and carbendazime; and especially cyprodinil, fenpropimorph, kresoxim-methyl, azoxystrobin, methyl 2-{2-[4-(3-trifluoromethylphenyl)-3-aza-2-oxa-4-pentenyl]-phenyl}-2-methoxyimino-acetate, acibenzolar-S-methyl and fenpropidine.
- 8. A method according to claims 4, 6 or 7 wherein component a) is compound I.01, or is compound I.03, or is compound I.05, or is compound I.06, or is compound I.07, or is compound I.08, or is compound I.09.
- 9. A fungicidal composition comprising a fungicidally effective combination of components a) and b) according to claim 1 together with an agriculturally acceptable carrier, and optionally a surfactant.
- 10. A composition according to claim 9 wherein the weight ratio of a) to b) is between 10:1 and 1:400.

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A. CLASSIFICATION OF SUBJECT MATTER //(A01N37/50,57:20,55:00,47:38,47:34,47:24,47:18, IPC 6 A01N37/50 //(A01N37/50,57:20,55:00,47:38,47:34,47:24,47:18, 47:04,43:88,43:84,43:82,43:76,43:653,43:56,43:54,43:50, 43:42,43:40,43:36,43:30,43:08,37:52,37:50,37:46,37:38,37:34,

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N IPC 6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category :	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Χ,Υ	WO 97 10716 A (BASF AG; BAYER HERBERT (DE); SAUTER HUBERT (DE); KOEHLE HARALD (DE) 27 March 1997  see page 1, line 4 - line 19  see page 3, line 29 - page 5, line 20  see page 11, line 23 - page 13, line 34  see page 24, line 1 - line 15  see page 43; example I.5  see page 44, line 1 - line 20  WO 97 06677 A (BASF AG; SCHWALGE BARBARA (DE); MUELLER RUTH (DE); BAYER HERBERT ()  27 February 1997  see page 1, line 6 - line 38  -/	1-10

X Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
23 December 1998	07/01/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk	Authorized officer
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	<del></del>		
A. CLASS IPC 6	37:24,37:20)		
According t	to International Patent Classification (IPC) or to both national classifi	lication and IPC	_
	SEARCHED		
	ocumentation searched (classification system followed by classifica		
	ation searched other than minimum documentation to the extent that $$		
Electronic a	data base consulted during the international search (name of data b	ase and, where practical, search terms	s used)
C DOCUM	ENTS CONSIDERED TO BE RELEVANT		
		<del></del>	<del></del>
Category *	Citation of document, with indication, where appropriate, of the re	elevant passages	Relevant to claim No.
Υ	WO 97 06678 A (BASF AG ;SCHWALGE (DE); MUELLER RUTH (DE); BAYER H 27 February 1997 see page 1, line 6 - page 5, lin	1-4,6, 8-10	
Υ	WO 97 06681 A (BASF AG ;SCHWALGE (DE); MUELLER RUTH (DE); BAYER H 27 February 1997 see page 1, line 6 - page 2, lin	1-4,7-10	
Υ	WO 97 06679 A (BASF AG ;SCHWALGE (DE); MUELLER RUTH (DE); BAYER H 27 February 1997 see page 1, line 6 - page 2, line	ERBERT ()	1-4,7-10
		-/	
	ner documents are listed in the continuation of box C.	X Patent family members are li	sted in annex.
"A" documer	regories of cited documents :  Int defining the general state of the art which is not ered to be of particular relevance	"T" later document published after the or priority date and not in conflict cited to understand the principle	with the application but
"E" earlier do filing da	ocument but published on or after the international ate	invention "X" document of particular relevance; cannot be considered novel or ca	the claimed invention
citation	nt which may throw doubts on priority claim(s) or s cifed to establish the publication date of another or other special reason (as specified) interested an oral disclosure, use, exhibition or	involve an inventive step when th "Y" document of particular relevance; cannot be considered to involve a	ne document is taken alone the claimed invention an inventive step when the
other m	neans nt published prior to the international filing date but an the pnority date claimed	document is combined with one of ments, such combination being of in the art.  "a" document member of the same pa	bvious to a person skilled
	ictual completion of the international search	Date of mailing of the international	
	3 December 1998		
Name and m	nailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL + 2280 HV Rijswijk	Authorized officer	
	Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3016	Lamers, W	

Inter chal Application No PCT/EP 98/05453

		PCT/EP 98/05453
C.(Continua	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category ·	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Υ	WO 97 06683 A (BASF AG ;SCHWALGE BARBARA (DE); MUELLER RUTH (DE); BAYER HERBERT () 27 February 1997 see page 1, line 6 - line 35	1-4,8-10
Y	WO 97 06684 A (BASF AG ;SCHWALGE BARBARA (DE); MUELLER RUTH (DE); BAYER HERBERT () 27 February 1997 see page 1, line 6 - page 2, line 5	1-4,8-10
Y	WO 97 06682 A (BASF AG ;SCHWALGE BARBARA (DE); MUELLER RUTH (DE); BAYER HERBERT () 27 February 1997 see page 1, line 6 - line 37	1-4,8-10
Y	DE 195 43 746 A (BASF AG) 28 May 1997 see page 2, line 5 - page 3, line 42 see page 11; table II.3E see page 17, line 25 - line 30 see page 18, line 25 - line 35	1-4,8-10
Y	WO 97 06680 A (BASF AG ;SCHWALGE BARBARA (DE); MUELLER RUTH (DE); BAYER HERBERT () 27 February 1997 see page 1, line 6 - line 43	1-4,8-10
Y	WO 97 00011 A (CIBA GEIGY AG ; KNAUF BEITER GERTRUDE (DE); ZEUN RONALD (DE)) 3 January 1997 see page 1 - page 3	1-4,8-10
Y	WO 97 15189 A (BASF AG ;HAMPEL MANFRED (DE); SCHELBERGER KLAUS (DE); LORENZ GISEL) 1 May 1997 see page 1, line 6 - line 33	1-4,8-10
Y	EP 0 741 970 A (SUMITOMO CHEMICAL CO) 13 November 1996 see page 2, line 20 - page 5, line 55	1-4,7-10
<b>Y</b>	WO 97 00012 A (CIBA GEIGY AG ;KNAUF BEITER GERTRUDE (DE); KUENG RUTH BEATRICE (CH) 3 January 1997 see page 1, paragraph 1 - paragraph 2 see page 2, line 20 - line 21	1-4,8-10
Y	WO 97 01277 A (CIBA GEIGY AG ; RUESS WILHELM (CH); KNAUF BEITER GERTRUDE (DE); KUE) 16 January 1997 see page 1, line 1 - page 2, line 3	1-4,7-10
Y	FR 2 740 005 A (RHONE POULENC AGROCHIMIE) 25 April 1997 see page 1, line 9 - page 2, line 13	1-4,8-10
	-/	

Inter anal Application No
PCT/EP 98/05453

		PCT/EP 98/05453
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category :	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Υ	FR 2 742 633 A (RHONE POULENC AGROCHIMIE) 27 June 1997 see page 1, line 4 - page 2, line 13	1-4,8-10
Y	"AZOXYSTROBIN COMPOSITIONS" RESEARCH DISCLOSURE, no. 390, October 1996, page 673/674 XP000639940 see the whole document	1-4,7-10
Υ	WO 97 03563 A (RHONE POULENC AGROCHIMIE; DUVERT PATRICE (FR)) 6 February 1997 see page 1, line 4 - page 2, line 19	1-4,8-10
Υ	WO 96 18299 A (BASF AG ;WAGNER OLIVER (DE); EICKEN KARL (DE); BAYER HERBERT (DE);) 20 June 1996 see page 1, line 6 - page 2, line 27	1-4,7-10
Y	EP 0 627 163 A (BAYER AG) 7 December 1994 see page 2, line 17 - line 33 see page 8, line 50 - page 9, line 23 see page 15, line 58 - page 16, line 29 see page 18, line 30 - line 45	1-4,8-10
Y	WO 96 03044 A (RHONE POULENC AGROCHIMIE; LATORSE MARIE PASCALE (FR)) 8 February 1996 see page 1, line 31 - page 2, line 9 see page 2, line 31 - page 3, line 2	1-5,8-10
Y	EP 0 610 764 A (BAYER AG) 17 August 1994 see page 2, line 11 - line 28 see page 6, line 14 - line 40	1-5,8-10
Y	WO 95 21154 A (BASF AG ;BAYER HERBERT (DE); SAUTER HUBERT (DE); MUELLER RUTH (DE)) 10 August 1995 cited in the application see the whole document	1-10
(	WO 95 18789 A (CIBA GEIGY AG ;FAROOQ SALEEM (CH); ZURFLUEH RENE (CH); ZIEGLER HUG) 13 July 1995 cited in the application see the whole document	1-10
<b>'</b>	WO 97 20809 A (CIBA GEIGY AG) 12 June 1997 cited in the application see the whole document	1-10
	-/	

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Interi nal Application No PCT/EP 98/05453

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT								
ategory	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.						
A	FRAINE DE P J ET AL: "A NEW SERIES OF BROAD-SPECTRUM BETA-METHOXYACRYLATE FUNGICIDES WITH AN OXIME ETHER SIDE-CHAIN" PESTICIDE SCIENCE, vol. 44, no. 1, May 1995, pages 77-79, XP002020496 see page 77, column 2, paragraph 2		1-10					
		·						

information on patent family members

Interr nal Application No
PCT/EP 98/05453

				PCT/EP	98/05453
Patent document cited in search report	t	Publication date		Patent family member(s)	Publication date
WO 9710716	Α	27-03-1997	AU	7212996 A	09-04-1997
			CA	2230140 A	27-03-1997
			CZ	9800881 A	12-08-1998
			EP	0859549 A	26-08-1998
	<b></b> -		PL	325972 A	17-08-1998
WO 9706677	Α	27-02-1997	AU	6702496 A	12-03-1997
			CA	2224288 A	27-02-1997
	•		CN	1193256 A	16-09-1998
			CZ	9800344 A	17-06-1998
			EP	0844817 A	03-06-1998
			PL 	324979 A	22-06-1998
WO 9706678	Α	27-02-1997	AU	6739696 A	12-03-1997
			EP	0844818 A	03-06-1998
WO 9706681	Α	27-02-1997	AU	6740896 A	12-03-1997
			EP 	0844820 A	03-06-1998
WO 9706679	Α	27-02-1997	AU	6788196 A	12-03-1997
			CA	2226745 A	27-02-1997
			CN	1193255 A	16-09-1998
			CZ	9800361 A	17-06-1998
			EP	0844823 A	03-06-1998
			PL 	324980 A	22-06-1998
WO 9706683	Α	27-02-1997	AU	6870496 A	12-03-1997
			EP	0844824 A	03-06-1998
WO 9706684	Α	27-02-1997	AU	6742296 A	12-03-1997
			EP	0844822 A	03-06-1998
WO 9706682	Α	27-02-1997	AU	6741796 A	12-03-1997
			EP	0844821 A	03-06-1998
DE 19543746	Α	28-05-1997	AU	7626896 A	19-06-1997
			CA	2235039 A	05-06-1997
			CZ	9801610 A	14-10-1998
			MO	9719595 A	05-06-1997
			EP	0863702 A	16-09-1998
WO <sup>-</sup> 9706680	Α	27-02-1997	AU	6740796 A	12-03-1997
			EP	0844819 A	03-06-1998
WO 9700011	Α	03-01-1997	AU	6300096 A	15-01-1997
			BR	9608356 A	18-08-1998
			CA	2221759 A	03-01-1997
			CZ	9704041 A	13-05-1998
			EP	0831697 A	01-04-1998
			PL 	323677 A	14-04-1998
WO 9715189	Α	01-05-1997 	AU	7291496 A	15-05-1997
EP 0741970	Α	13-11-1996	JP	7157403 A	20-06-1995
			JP	7187917 A	25-07-1995
			JP	7285811 A	31-10-1995
			JP JP	7285812 A 7304607 A	31-10-1995

information on patent family members

Intern al Application No
PCT/EP 98/05453

Patent document cited in search repor	t	Publication date		ent family ember(s)	Publication date
EP 0741970	A		JP JP JP JP AU WO	7304606 A 7316004 A 7324008 A 8026920 A 8026912 A 1120495 A 9515083 A	21-11-1995 05-12-1995 12-12-1995 30-01-1996 30-01-1996 19-06-1995 08-06-1995
WO 9700012	Α	03-01-1997	AU AU BR CA CZ EP PL	690464 B 6125196 A 9608358 A 2224977 A 9704040 A 0831698 A 323945 A	23-04-1998 15-01-1997 18-08-1998 03-01-1997 13-05-1998 01-04-1998 27-04-1998
WO 9701277	Α	16-01-1997	AU AU CA CZ EP PL	690469 B 6358796 A 2220114 A 9704199 A 0836385 A 323674 A	23-04-1998 30-01-1997 16-01-1997 13-05-1998 22-04-1998 14-04-1998
FR 2740005	Α	25-04-1997	NONE		
FR 2742633	Α	27-06-1997	NONE		
WO 9703563	А	06-02-1997	FR AU CA CN EP HR	2737086 A 6662896 A 2224890 A 1193890 A 0841853 A 960351 A	31-01-1997 18-02-1997 06-02-1997 23-09-1998 20-05-1998 28-02-1998
WO 9618299	A	20-06-1996	DE AU BG BR CA CN CZ EP HU JP PL	4444911 A 689684 B 4260196 A 101538 A 9510048 A 2208141 A 1170336 A 9701823 A 0797386 A 77788 A 10510285 T 320592 A	27-06-1996 02-04-1998 03-07-1996 28-11-1997 16-06-1998 20-06-1996 14-01-1998 13-05-1998 01-10-1997 28-08-1998 06-10-1998 13-10-1997
EP 0627163	3 A	07-12-1994	DE AT AU AU BR CN DE DK ES GR	4318285 A 141131 T 669981 B 6327694 A 9402152 A 1099552 A 59400489 D 627163 T 2091068 T 3020827 T 67195 A	08-12-1994 15-08-1996 27-06-1996 08-12-1994 27-12-1994 08-03-1995 19-09-1996 02-12-1996 16-10-1996 30-11-1996

...formation on patent family members

Interr nal Application No PCT/EP 98/05453

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 9518789	A	LV 11684 B MD 960291 A NO 962823 A NZ 278385 A SG 45424 A SK 88096 A ZA 9500027 A BR 9503066 A	20-06-1997 31-10-1997 04-07-1996 25-03-1998 16-01-1998 04-12-1998 26-07-1995 27-02-1996	
WO 9720809	A 12-06-1997	AU 1066297 A CA 2238632 A CZ 9801732 A EP 0865424 A	27-06-1997 12-06-1997 12-08-1998 23-09-1998	

information on patent family members

PCT/EP 98/05453

Patent document cited in search report		Publication date		ent family ember(s)	Publication date
EP 0627163	A		JP NZ PL US US US	7089812 A 260622 A 303659 A 5439926 A 5569656 A 5639774 A 5736551 A 9403812 A	04-04-1995 26-05-1995 09-01-1995 08-08-1995 29-10-1996 17-06-1997 07-04-1998 30-01-1995
WO 9603044	Α	08-02-1996	FR AU BG BR CZ EP HU JP PL SK ZA	2722652 A 3080595 A 101231 A 9508792 A 2192989 A 9700180 A 0773720 A 77234 A,B 10503192 T 318328 A 8697 A 9505935 A	26-01-1996 22-02-1996 28-11-1997 30-12-1997 08-02-1996 16-04-1997 21-05-1997 02-03-1998 24-03-1998 09-06-1997 10-09-1997 20-02-1996
EP 0610764	A	17-08-1994	DE BR CN HU JP PL US US US	4304172 A 9400484 A 1091238 A 66297 A,B 6247810 A 302198 A 5491165 A 5650423 A 5776976 A 9400947 A	25-08-1994 27-09-1994 31-08-1994 28-11-1994 06-09-1994 22-08-1994 13-02-1996 22-07-1997 07-07-1998 25-08-1994
WO 9521154	Α	10-08-1995	AU AU BR CA CN CZ EP HU JP NZ PL SK	681932 B 1416095 A 9506720 A 2182407 A 1152908 A 9602315 A 0741694 A 75534 A 9509410 T 278072 A 318595 A 102396 A	11-09-1997 21-08-1995 23-09-1997 10-08-1995 25-06-1997 11-12-1996 13-11-1996 28-05-1997 22-09-1997 26-02-1998 23-06-1997 05-03-1997
WO 9518789	Α	13-07-1995	US AU BG CA CN CZ EP FI HU JP LV	5756426 A 690190 B 1385195 A 100760 A 2179418 A 1141032 A 9601990 A 0738260 A 962712 A 74980 A 9511484 T 11684 A	26-05-1998 23-04-1998 01-08-1995 31-03-1997 13-07-1995 22-01-1997 16-10-1996 23-10-1996 16-08-1996 28-03-1997 18-11-1997 20-02-1997